

Van der Waals complexes between carbonyl fluoride and boron trifluoride observed in liquefied argon, krypton, and nitrogen: A FTIR and ab initio study

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Abstract

The IR spectra (4000-400 cm^{-1}) of COF_2/BF_3 mixtures, dissolved in liquefied argon (LAr), krypton (LKr), and nitrogen (LN_2), have been examined. In all spectra evidence was found for the formation of a 1:1 van der Waals complex. Using spectra recorded at several temperatures between 81 and 172 K the complexation enthalpies ΔH° in LAr, LKr, and LN_2 were determined to be -11.8(3), -10.6(3), and -7.8(3) kJ mol^{-1} , respectively. A theoretical study, using both density functional theory at the B3LYP/6-311++G(d,p) level and ab initio at the MP2/aug-cc-pVTZ level, indicates that the complexation can occur either via the oxygen or via a fluorine atom of COF_2 . From a comparison of the experimental and calculated frequencies it was concluded that the observed complex bands are due to a species in which the boron atom coordinates with the oxygen lone pairs. The complexation energy $\Delta(c)E$ is obtained from the ΔH° by correcting for solvent influences, and thermal contributions equals -15.0(6) kJ mol^{-1} . This value agrees well with the MP2/aug-cc-pVTZ level result, -12.4 kJ mol^{-1} . The complexation entropy ΔS° has been found to be influenced by the solvent and is correlated with ΔH° . This correlation reflects the existence of the compensation effect for the thermodynamics of van der Waals complexes.

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